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We present calculated cross sections for elastic and inelastic collisions of low-energy electrons with octafluorocyclobutane, $c\text{-C}_4\text{F}_8$. The integral elastic cross section displays a rich resonance structure, which we analyze in terms of temporary trapping in virtual valence orbitals. The differential elastic cross sections compare well with recent measurements at energies where the approximations used in the calculations are expected to be valid. Integral and differential cross sections for electron-impact excitation of the lowest singlet and triplet excited states were obtained. We relate the small magnitude of the inelastic integral cross sections and the unusual form of the inelastic differential cross sections to the symmetries of the electronic states involved in the transition.

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I. INTRODUCTION

Octafluorocyclobutane ($c\text{-C}_4\text{F}_8$) is a common feed gas for low-temperature plasma etching of silicon dioxide, a key step in the manufacture of semiconductor microelectronics. Because typical electron kinetic energies in processing plasmas range from less than 1 electron volt (eV) to a few tens of eV, knowledge of the cross sections for low-energy electron-molecule collision processes is essential to an understanding of plasma behavior. However, for $c\text{-C}_4\text{F}_8$, only limited cross section data exist in the literature, though the situation has begun to improve. A derivative electron transmission spectrum, sensitive to resonance features in the total scattering cross section, was measured some years ago by Ishii *et al.*¹ Measurements of the total scattering cross section itself were recently obtained by Moore *et al.*² and by Nishimura *et al.*,³ while Tanaka *et al.*⁴ recently obtained the first measurements of the elastic electron cross section. Electron-impact ionization cross sections, including fragment-ion production cross sections, have been reported by Bibby and Carter,⁵ Kurepa,⁶ Sugai *et al.*,⁷ and Haaland *et al.*⁸ The differences between the two recent sets^{7,8} of ionization cross sections are considerable; both agree qualitatively with the relative measurements of Lifshitz and Grajower⁹ below 20 eV, but the measurements of Sugai *et al.* are in better agreement with the earlier single-point determination of the total ionization cross section at 70 eV by Beran and Kevan,¹⁰ especially if the data of Beran and Kevan are renormalized as has been suggested.¹¹ Sugai *et al.*⁷ also reported cross sections for neutral-fragment production, but subsequent measurements on other molecules that Sugai *et al.* studied by the same technique have called into question the reliability of their neutral-dissociation cross sections.^{12,13} The neutral excitation/dissociation cross sections thus remain one of the areas of greatest uncertainty.

Electron attachment to $c\text{-C}_4\text{F}_8$ has been studied extensively.^{5,8,9,14–24} Many of these studies focused on the nondissociative attachment of electrons at very low energies, forming metastable C_4F_8^- ions with a lifetime of 10 μs or more,^{14,17,21} the large cross section for this process accounts

for the excellent dielectric properties of $c\text{-C}_4\text{F}_8$. At higher energies, several resonant peaks are observed in dissociative attachment, with F^- being by far the principal ionic fragment produced,⁵ although larger anions are also formed. Swarm parameters (drift velocities and ionization and attachment coefficients) were measured by Naidu *et al.*²⁵ Yamaji *et al.*²⁶ have also carried out swarm measurements on dilute mixtures of $c\text{-C}_4\text{F}_8$ in argon.

In this paper, we report differential and integral elastic electron scattering cross sections as well as electron-impact excitation cross sections for two low-lying electronic states. These cross sections are calculated *ab initio* using the Schwinger multichannel (SMC) method.^{27,28} As will be seen, our differential elastic cross sections compare favorably with the measurements of Tanaka *et al.* at those energies where the static-exchange approximation is expected to work well. Symmetry decomposition of the integral elastic cross section reveals several shape resonances. We discuss the origin of these resonances and their relation to features seen in dissociative attachment. The qualitative features of the inelastic cross sections will be analyzed on the basis of symmetry considerations.

II. COMPUTATIONAL DETAILS

The SMC method and its implementation for parallel computers have been described elsewhere.^{27–30} Here we give only details particular to the present calculations.

The equilibrium geometry of $c\text{-C}_4\text{F}_8$ was optimized within the D_{2d} point group using GAUSSIAN 94³¹ at the second-order Möller–Plesset perturbation theory level within the 6-31G(*d*) basis set internal to Gaussian. With core orbitals frozen, or MP2(FC)/6-31G(*d*) in the usual notation, we obtained nearly the same geometry as with the full set included in the MP2 calculation, i.e., MP2(FU)/6-31G(*d*). The former geometry was used for the inelastic calculations and the latter for the elastic calculations. The elastic cross sections were obtained using the 6-311+G(2*d*) basis set internal to the program system GAMESS³² to describe both bound and scattering orbitals, with default choices for the

exponents and splitting factors of the supplementary functions. Both GAMESS and the SMC program retain all six Cartesian components of the d orbitals, so the $c\text{-C}_4\text{F}_8$ basis set comprised in aggregate 504 primitive and 348 contracted Cartesian Gaussian functions.

Inelastic calculations employed the 6-311+G(d) basis, i.e., the same basis as the elastic calculations except that a single d orbital per atom (whose exponent is the geometric mean of the exponents in the $2d$ sets) was used, giving a total of 432 primitive and 236 contracted Cartesian Gaussian basis functions. The excited states were described as single configurations via the improved virtual orbital (IVO) method,³³ which produced thresholds for the triplet and singlet states of 9.45 and 9.75 eV, respectively. For comparison, single-excitation configuration–interaction (SECI) calculations using the 6-31+G(d) basis set and GAUSSIAN 98³⁴ produced thresholds of 8.52 and 9.13 eV, respectively, for the triplet and singlet states.

The SMC method employs a three-dimensional numerical quadrature in momentum space for the representation of the Green's function. The sufficiency of this quadrature may be assessed in part from the agreement between the two components of the 2E representation in the integral elastic cross section. Because these two components are not equivalent with respect to the angular layout of the quadrature points, good agreement between them implies that the quadrature is well converged in at least the two angular dimensions. As a further check on the elastic results, static-exchange results were also calculated at the MP2(FC)/6-31G(d) geometry using smaller quadratures both with the 6-311+G($2d$) basis set and with an independent basis set, the latter consisting of the TZV basis internal to GAMESS together with a $1s1p2d$ diffuse/polarization supplement on each atom, again with default exponents and splitting parameters; this basis set comprised 540 primitive and 360 contracted Cartesian Gaussians. Agreement was very close except in 2E symmetry, where both resonant and nonresonant scattering, as well as the interference between the two, appeared quite sensitive to the radial quadrature employed. The smaller calculations employed 32 Gauss–Legendre points in $|\vec{k}|$ below 3.0 atomic units (a.u.), corresponding to $E=122$ eV, and 40 Gauss–Laguerre points above $|\vec{k}|=3.0$ a.u. The final results presented here used a much denser mesh at low energies, consisting of 32 Gauss–Legendre quadrature points below $|\vec{k}|=2$ a.u. ($E=54.4$ eV) and 50 Gauss–Laguerre points above. Reducing the quadrature from 50 to 40 Gauss–Laguerre points resulted in only minor changes in the cross section. Because the inelastic calculations employed both a smaller quadrature and a smaller basis set than the elastic calculations, we anticipate that the excitation cross sections reported below will be somewhat less accurate than the elastic cross section.

III. RESULTS AND DISCUSSION

In Fig. 1, we present the symmetry components of the integral elastic cross section. Note that we show both components of 2E rather than their sum. Since these should be identical, any disagreement between them reflects quadrature

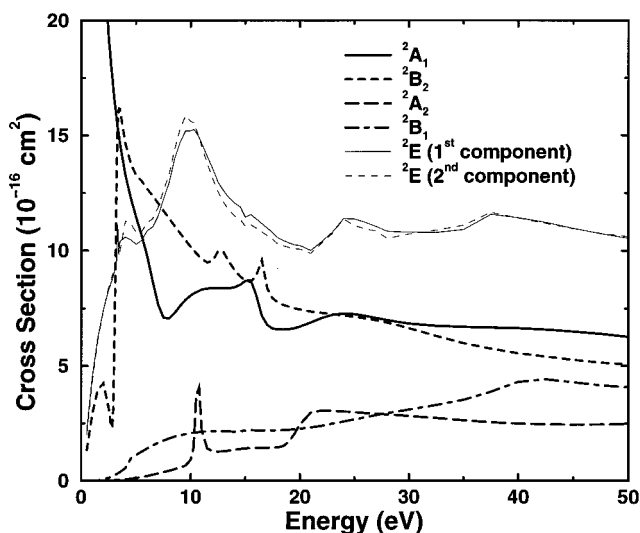


FIG. 1. Symmetry components of the static-exchange elastic integral cross section for electron collisions with $c\text{-C}_4\text{F}_8$.

limitations or other numerical error, but as may be seen, the agreement is generally quite good. Below 5 eV, there is a rise in the totally symmetric (2A_1) component. This rise is characteristic of the static-exchange approximation, which omits the net-attractive polarization potential, and consequently does not imply a similar rise in the actual elastic cross section. Above 5 eV, the static-exchange approximation is increasingly reliable, although resonances are, because of the increased interaction time, especially sensitive to polarization; the static-exchange approximation therefore tends to locate them too high in energy, typically by 2 to 4 eV.

The multiple peaks and windows evident in Fig. 1 reflect a rich resonance structure. Phase-shift analysis is helpful in assigning positions and widths to these resonances. Eigenphase sums for the four resonant representations are shown in Fig. 2, together with nonlinear least-squares fits over the corresponding energy ranges. The fits employed a cubic polynomial to represent the background phase shift and either two or three arctangent functions to account for the resonant phase jumps. In all but the 2A_1 representation, the fits were constrained to give zero phase shift at zero energy, in order to reflect the suppression of scattering by the angular momentum barriers. Results of this fitting procedure are shown in Table I. It should be noted that one obtains nearly as good a fit, judged by the sum of the squared residuals, if one assumes only two 2E resonances between 0 and 20 eV rather than three, with the two-resonance fit placing resonances at 8.25 and 14.0 eV. Thus, although we prefer the three-resonance fit shown in Table I and Fig. 2 because it accords better both with the peak structure visible in Fig. 1 and with the molecular-orbital considerations discussed immediately below, it cannot be taken as conclusive.

Comparing the resonance assignments of Table I with the cross section components of Fig. 1, we see that in most cases it is possible to associate a resonance with a cross section peak or shoulder. However, in some cases, notably those of the 2B_2 resonance at 3.0 eV and the 2A_1 resonance

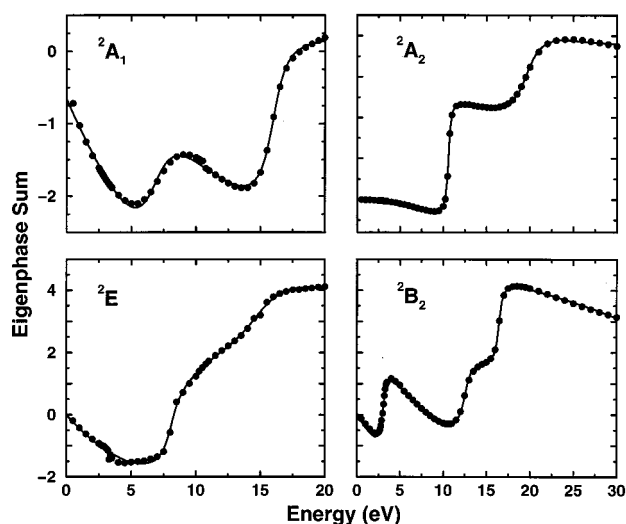


FIG. 2. Eigenphase sums in the four resonant symmetries. The curves are obtained by fitting to the computed values, shown by the circles, as described in the text. Only one component of the degenerate 2E representation is shown.

at 6.8 eV, we find asymmetric profiles rather than simple enhancements. Such asymmetric profiles may arise, when the background phase shift is large, as the interference between resonant and direct scattering changes from destructive to constructive, or *vice versa*, over the resonance profile.

We may compare the energies and symmetries of our calculated resonances with expectations derived from an elementary but powerful model, in which shape resonances arise from temporary trapping in empty valence orbitals, usually antibonding in character (e.g., Ref. 35); with electron-transmission measurements;¹ and with the results of dissociative attachment experiments. In making the last-mentioned comparisons, one must bear in mind not only the shift to *higher* energy typical of the static-exchange approximation but also the lifetime effect that typically causes a resonance maximum in dissociative attachment to appear shifted to *lower* energy than the corresponding resonance in the elastic scattering cross section.³⁶ In the simplest picture, we would expect a saturated halocarbon such as $c\text{-C}_4\text{F}_8$ to exhibit a shape resonance associated with the empty valence orbital conjugate to each bonding orbital. This picture is sufficient to explain the number and the symmetry of the low-energy

TABLE I. Resonance positions and widths obtained from the eigenphase-sum fits shown in Fig. 2.

Symmetry	Position (eV)	Width (eV)
2A_1	6.8	2.9
	16.0	1.8
2B_2	3.0	0.33
	12.5	1.3
	16.4	0.70
2A_2	10.6	0.23
	19.6	3.2
2E	8.1	1.2
	10.0	5.8
	14.7	3.9

TABLE II. Minimal-basis-set (STO-6G) virtual orbitals of $c\text{-C}_4\text{F}_8$.

Symmetry	Energy (eV)	Principal character
a_1	13.5	C-F σ^*
	20.8	C-F σ^*
b_2	9.8	C-F σ^*
	15.8	C-F σ^*
a_2	20.6	C-C σ^*
	14.5	C-C σ^*
e	12.7	C-C σ^*
	15.5	C-F σ^*
	16.6	C-F σ^*

shape resonances in elastic scattering by molecules as large as C_3F_8 .³⁷ In the case of $c\text{-C}_4\text{F}_8$, we would anticipate 2B_2 , 2A_2 , and 2E resonances of C-C antibonding character, together with two 2A_1 , two 2B_2 , and two 2E resonances of C-F antibonding character, for a total of nine (three fewer than the number of bonds because the 2E resonances are doubly degenerate). Consistent with this model, qualitative information about expected resonance energies may be obtained from the minimal-basis-set (STO-6G) Hartree-Fock energies in Table II, computed using GAMESS.³² Comparing Tables I and II, we see that the minimal-basis orbitals predict the number and symmetry assignment of the resonances quite well; moreover, if we shift the virtual orbital energies down by 4 or 5 eV, they are in fair agreement with the calculated resonance positions.

An apparent exception occurs in 2A_2 symmetry, where there are two resonances but only one virtual valence orbital. However, returning to Fig. 1, we see that there are maxima suggestive of additional high-energy resonances near 24 eV in 2A_1 and 2E , and a shoulder at about the same energy in 2B_2 , as well as features around 38 to 40 eV in 2E , 2B_1 , and possibly 2A_1 that may indicate still higher-lying resonances. The “extra” resonance in 2A_2 thus appears to be merely the lowest lying of a group of higher-energy shape resonances that do not correlate with virtual valence orbitals.

Experimental data on dissociative attachment to $c\text{-C}_4\text{F}_8$ are summarized in Table III. As may be seen, there is a reasonable consensus on the existence of five resonance maxima located at approximately 4, 5, 7, 8, and 10 eV. Allowing for the lifetime effect in dissociative attachment and the upward energy shift of static-exchange resonances, we

TABLE III. Observed dissociative-attachment maxima in $c\text{-C}_4\text{F}_8$.

Energy (eV)				
Ref. 5	Ref. 17	Ref. 9	Ref. 21	Anion(s) observed ^a
		1.75		F^- , C_3F_5^-
		3.75		C_3F_5^-
4.3	4.35	4.3–4.4	4.1	F^- , CF_3^- , C_2F_3^- , C_3F_5^-
5.0	4.95		4.8–4.9	F^- , F_2^- , CF_2^- , CF_3^-
6.8	7.4	6.75	6.5	F^-
8.0	8.5–8.8	8.2	7.9	F^- , F_2^- , CF_2^- , C_2F_3^-
9.6				F^-
10.3	10.4–11.2	10.5	10.2	F^- , F_2^- , CF_2^-

^aWhere more than one product is listed, not all are necessarily seen in each measurement.

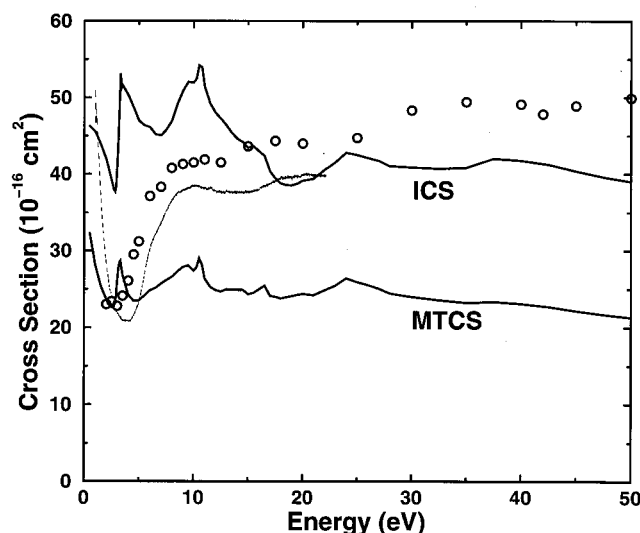


FIG. 3. Integral elastic cross section (ICS) and momentum transfer cross section (MTCS) computed for $c\text{-C}_4\text{F}_8$ in the static-exchange approximation. Also shown for comparison are the measured total scattering cross sections of Ref. 2 (dashed line) and Ref. 3 (circles).

might make a very tentative association between these features and the calculated elastic resonances at 6.8, 8.1, 10.0, 10.6, and 12.5 eV. A small point in favor of this association is that the corrections needed cluster rather closely around an average of 2.8 eV, which is of reasonable size. Moreover, shifting the 2B_2 resonance downward from its static-exchange position of 3.0 eV by the same amount would be consistent with the observation of strong nondissociative attachment near zero impact energy.

Electron-transmission measurements,¹ in which the derivative of the transmitted current is monitored, indicate the presence of a resonance at 4.9 eV. On the basis of their own minimal-basis-set calculations, Ishii *et al.* assign this resonance as 2E , which is consistent with our own minimal-basis-set results (Table II) and may indeed be correct; however, the foregoing discussion suggests as a possible alternative assignment the 2A_1 resonance placed by the static-exchange calculation at 6.8 eV. Ishii *et al.* saw indications in their experiments of the nondissociative attachment at very low energies that has been widely observed, and like us they associated it with the lowest valence virtual orbital of b_2 symmetry.

The elastic integral cross section (ICS) for $c\text{-C}_4\text{F}_8$ obtained by summing the symmetry components is shown in Fig. 3 together with the momentum-transfer cross section (MTCS). Both the ICS and the MTCS show an artifactual rise at low energy whose origin was discussed above, while between 5 and 20 eV the resonances that we have discussed give rise to undulations. No experimental values of either cross section are available for comparison. Novak and Fr  chette¹¹ and Itoh *et al.*³⁸ arrived at similar estimates of the MTCS based on electron swarm measurements.²⁵ The MTCS of Itoh *et al.* has constant values of $80 \times 10^{-16} \text{ cm}^2$ below 4 eV and $14 \times 10^{-16} \text{ cm}^2$ above 11 eV, with a smooth interpolation in between, and is thus much larger than the present MTCS at low energy and much smaller at high energy.

Also shown in Fig. 3 for comparison are the total cross

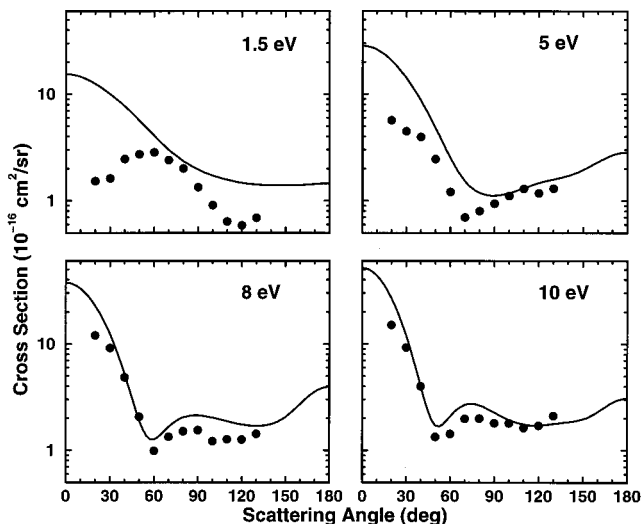


FIG. 4. Differential cross section for elastic scattering of electrons by $c\text{-C}_4\text{F}_8$ at the energies indicated on the figure. Solid line: present calculation; circles: measurements of Nishimura *et al.*, Ref. 3.

sections (TCS) measured by Sanabia *et al.*² and by Nishimura *et al.*,³ which above 4 eV are similar in form but different in magnitude. The result of Nishimura *et al.* appears more consistent with the present elastic ICS at energies above 15 eV, where the static-exchange approximation should work reasonably well. At lower energies, however, the present elastic cross section is considerably larger than either measured TCS. Most of the disagreement is probably attributable to the artifactual enhancement of low-energy s -wave scattering and the upward shift in resonance energies resulting from the static-exchange approximation, which we have already discussed, as well as to the tendency of fixed-nuclei calculations to produce resonances that are too sharp. The total cross sections exhibit a broad maximum near 10 eV that may correlate with the peak produced nearby in our elastic cross section by several overlapping shape resonances. There also appears to be a broad peak or plateau in the TCS at 18 to 20 eV where no similar structure in the summed elastic ICS is present; however, at these energies electronic excitation and ionization processes may make a significant contribution to the TCS.

In Figs. 4 and 5, we compare our calculated elastic DCS with the measurements of Tanaka *et al.*⁴ At low energies, the static-exchange values are, as expected, both qualitatively and quantitatively different from the experimental values; however, the agreement becomes increasingly good at higher energies. Indeed, the qualitative agreement is quite good from 8 eV upward. The largest percentage disagreements tend to be at local minima, where the absolute magnitude of the DCS is rather small; the largest absolute disagreements occur in the near-forward direction at low energies, where it appears that polarization is needed to obtain the suppression of the cross section seen experimentally.

We turn now to electron-impact excitation. The highest occupied molecular orbital (HOMO) of $c\text{-C}_4\text{F}_8$ belongs to b_1 , while, as indicated in Table II, the lowest unoccupied molecular orbital (LUMO) belongs to b_2 ; thus the

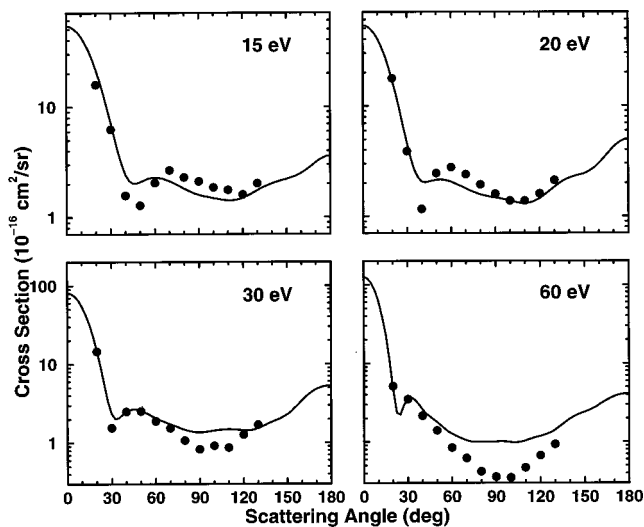
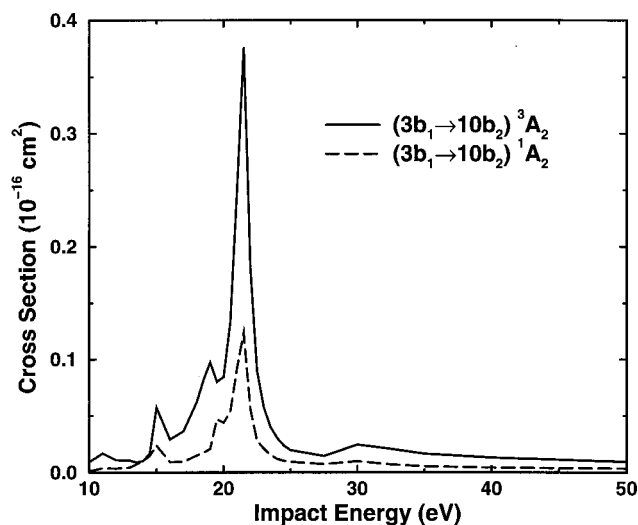
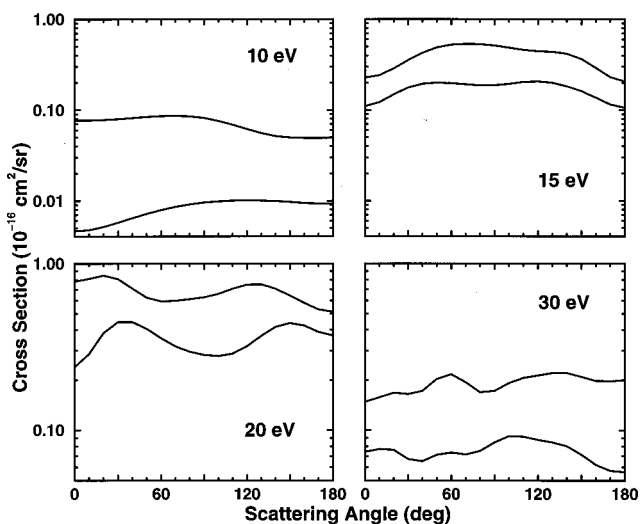


FIG. 5. As in Fig. 4, at higher energies.

HOMO→LUMO excitation leads to 3A_2 and 1A_2 excited states. Integral and differential cross sections for these transitions are shown in Figs. 6 and 7. From Fig. 6, we see that the integral cross sections are quite small, being less than $0.1 \times 10^{-16} \text{ cm}^2$ except in a narrow energy range around 22 eV, while the differential cross sections have an unusual form, with local minima at 0° (forward scattering) and 180° (backward scattering).

The $X\ ^1A_1 \rightarrow 1\ ^{1,3}A_2$ transition is symmetry disfavored: if the collision plane coincides with either of the two perpendicular mirror planes containing the molecular \hat{C}_2 axis, the excitation process is forbidden by symmetry, and by continuity, it can be expected that the cross section will be small at nearby scattering geometries. An analogous situation has been studied in formaldehyde, H_2CO ,^{39,40} where it was found that the integral cross sections for the $\tilde{a}\ ^3A_2$ and $\tilde{A}\ ^1A_2$ excitations were unusually small, and that the differential

FIG. 6. Integral cross sections for the $X\ ^1A_1 \rightarrow 1\ ^{1,3}A_2$ electron-impact excitation processes in $c\text{-C}_4\text{F}_8$. Dashed line, $1\ ^1A_2$ channel; solid line, $1\ ^3A_2$ channel.FIG. 7. Differential cross sections for the $X\ ^1A_1 \rightarrow 1\ ^{1,3}A_2$ electron-impact excitation processes in $c\text{-C}_4\text{F}_8$ at selected energies. Lower line: $1\ ^1A_2$ channel; upper line: $1\ ^3A_2$ channel.

cross sections showed scattering to be suppressed in the forward and backward directions. The latter observation is connected to the symmetry rule stating that the differential cross sections for $\Sigma^+ \leftrightarrow \Sigma^-$ transitions in diatomics must vanish in the forward and backward directions.⁴¹ Because in H_2CO and $c\text{-C}_4\text{F}_8$ there are only two, rather than an infinite number, of reflection planes containing the symmetry axis, the forward and backward excitation cross sections are reduced but not entirely suppressed.

The inelastic collision calculations were carried out in the C_{2v} subgroup of the full D_{2d} point group. When the integral cross section is decomposed into representations of C_{2v} , the peak near 22 eV in both the 3A_2 and the 1A_2 cross sections is found to arise from the 2A_1 component of C_{2v} , which comprises the 2A_1 and 2B_2 representations of D_{2d} . If this peak arises from a core-excited shape resonance built on an A_2 core, the orbital involved would therefore be of either a_2 or b_1 symmetry, using D_{2d} labeling. It is also possible, however, especially given the small overall magnitude of the $^{1,3}A_2$ cross sections, that the peak is a pseudoresonance associated with higher-lying excitation channels that should be, but are not, open at this energy, and is thus purely numerical in origin. More extensive calculations will be required to determine its character.

IV. SUMMARY AND CONCLUSION

We have reported calculated elastic and inelastic cross sections for low-energy electron collisions with $c\text{-C}_4\text{F}_8$. The elastic cross sections are in fair agreement with the experimental elastic DCS at energies where the static-exchange approximation employed in the present work is expected to be reliable. Numerous resonances are observable in the elastic cross section. Those occurring at low energy can be associated with virtual valence orbitals and correlate fairly well with features seen in dissociative attachment if an energy shift of 2.8 eV is applied. The lowest resonance, which falls at 3.0 eV in the static-exchange approximation, appears to be

associated with nondissociative attachment of very slow electrons to form metastable $c\text{-C}_4\text{F}_8^-$ ions. The integral cross sections for the HOMO→LUMO electronic-excitation process leading to 3A_2 and 1A_2 excited states are found to be quite small, while the corresponding differential cross sections are unusual in form, with local minima at 0° and 180° . These properties of the excitation cross sections may be understood on the basis of symmetry considerations first developed in connection with diatomic⁴¹ and small polyatomic^{39,40} molecules.

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